

CHM 3411 – Problem Set 7

Due date: Monday, March 4th The second hour exam is on Friday, March 8th. It will cover all of Chapter 9, and sections 10.1 to 10.5 of Chapter 10, plus handouts.

Do all of the following problems. Show your work.

“To understand something means to derive it from quantum mechanics, which nobody understands.” - unknown

1) Consider the following function as a “guess” for the solution to the TISE for the particle in a box.

$$f(x) = N(Lx - x^2) \quad 0 \leq x \leq L \quad (1.1)$$

$$f(x) = 0 \quad x < 0 \text{ or } x > L$$

- What value for N makes $f(x)$ a normalized function?
- What is the value for E_f , the energy corresponding to the function $f(x)$?
- The exact solution for the energy of the ground state of a particle in a box is

$$E(n=1) = \frac{\hbar^2}{8mL^2} \quad (1.2)$$

Is the value for E_f found in part b consistent with the variational principle? Explain.

2) In pure sp^3 hybridization, the following hybrid orbitals can be constructed from atomic orbitals of an atom

$$h_1 = N(s + p_x + p_y + p_z) \quad h_3 = N(s - p_x + p_y - p_z)$$

$$h_2 = N(s - p_x - p_y + p_z) \quad h_4 = N(s + p_x - p_y - p_z)$$

- Find the value for N that makes $h_1 - h_4$ normalized functions.
- Find the values for the following two integrals.

$$\int (h_1)(h_2) d\tau$$

$$\int (h_1)(p_x) d\tau$$

- Based on your answer in part b, are h_1 and h_2 orthogonal? Why or why not?
- Based on your answer in part b, are h_1 and p_x orthogonal? Why or why not?

3) A water molecule (H_2O) has three nuclei and 10 electrons.

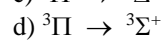
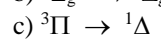
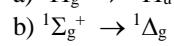
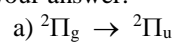
a) If we write down the complete TISE for a water molecule, how many terms will we have for each of the following: 1) kinetic energy for the nuclei, 2) kinetic energy for the electrons, 3) nuclear-nuclear potential energy, 4) nuclear-electron potential energy, 5) electron-electron potential energy.

b) If we try and solve the TISE for a water molecule using the Born-Oppenheimer approximation, how are each of the energy terms in a affected? If making the Born-Oppenheimer approximation has no effect on a particular energy term, say “no effect” as your answer.

4) Give the electron configuration and all of the term symbols corresponding to the following diatomic molecules and ions. For cases where more than one electronic state can arise for a particular electron configuration, rank the electronic states in order from lowest to highest energy. You do not have to assign +/- symmetry for any of the Σ electronic states you find.

- C_2
- B_2^+
- CN
- CN^-

5) Which of the following electronic transitions in diatomic molecules are allowed, and which are forbidden? For the forbidden transitions, list all of the selection rules that are violated. Also indicate which electronic transitions are taking place in homonuclear diatomic molecules, and which are taking place in heteronuclear diatomic molecules. Justify your answer.



Solutions.

1) a) Normalization means

$$\begin{aligned}
 1 &= \int_0^L [N(Lx - x^2)]^2 dx = N^2 \int_0^L [L^2x^2 - 2Lx^3 + x^4] dx \\
 &= N^2 [(L^2x^3/3) - (2Lx^4/4) + (x^5/5)]_0^L \\
 &= N^2 [(L^5/3) - (L^5/2) + (L^5/5)] = N^2L^5/30 \quad \text{so } N = (30/L^5)^{1/2}
 \end{aligned}$$

$$\begin{aligned}
 \text{b) } E_f &= \int_0^L [(30/L^5)^{1/2} (Lx - x^2)] (- (\hbar^2/2m) d^2/dx^2) [(30/L^5)^{1/2} (Lx - x^2)] dx \\
 &= - (30/L^5) (\hbar^2/2m) \int_0^L (Lx - x^2) (-2) dx \\
 &= \frac{30\hbar^2}{mL^5} \int_0^L (Lx - x^2) dx = \frac{30\hbar^2}{mL^5} [(Lx^2/2) - (x^3/3)]_0^L \\
 &= \frac{30\hbar^2}{mL^5} \frac{L^3}{6} = \frac{5\hbar^2}{mL^2} = \frac{5\hbar^2}{4\pi^2mL^2} = (h^2/mL^2) (5/4\pi^2) = 0.12665 (h^2/mL^2)
 \end{aligned}$$

c) The exact value for energy is $E(n=1) = (1/8) (h^2/mL^2) = 0.125 (h^2/mL^2)$

Based on the variational theorem, we expect $E_f \geq E(n=1)$, which in fact is the case. So our result is consistent with the variational theorem.

What is interesting is that our trial wavefunction gives a result that is close to the exact result (it differs by 1.3 %). In a real variational calculation we would not know the “exact” result (if we did, why do a variational calculation?) but the result here suggests the variational method works well.

2) a) Normalization for h_1 is the requirement

$$\begin{aligned}
 1 &= \int h_1 h_1 d\tau = \int [N(s + p_x + p_y + p_z)]^2 d\tau \\
 &= N^2 \int (s + p_x + p_y + p_z) (s + p_x + p_y + p_z) d\tau \\
 &= N^2 \int (s s + s p_x + s p_y + s p_z + p_x s + p_x p_x + p_x p_y + p_x p_z + p_y s + p_y p_x + p_y p_y + p_y p_z \\
 &\quad + p_z s + p_z p_x + p_z p_y + p_z p_z) d\tau
 \end{aligned}$$

Since $s, p_x, p_y,$ and p_z are orthonormal functions, the above gives

$$= N^2 (1 + 0 + 0 + 0 + 0 + 1 + 0 + 0 + 0 + 0 + 1 + 0 + 0 + 0 + 0 + 1) = 4N^2$$

and so $N = (1/2)$

It is clear we will obtain the same result for $h_2, h_3,$ and $h_4,$ so in all cases the normalization constant is $1/2$.

$$\begin{aligned}
 \text{b) } \int (h_1) (h_2) d\tau &= \int [(1/2) (s + p_x + p_y + p_z)] [(1/2) (s - p_x - p_y + p_z)] d\tau \\
 &= (1/4) \int (s s - s p_x - s p_y + s p_z + p_x s - p_x p_x - p_x p_y + p_x p_z + p_y s - p_y p_x - p_y p_y + p_y p_z \\
 &\quad + p_z s - p_z p_x - p_z p_y + p_z p_z) d\tau \\
 &= (1/4) (1 + 0 + 0 + 0 + 0 - 1 + 0 + 0 + 0 + 0 - 1 + 0 + 0 + 0 + 0 + 1) = 0
 \end{aligned}$$

$$\int (h_1) (p_x) d\tau = \int [(1/2) (s + p_x + p_y + p_z)] (p_x) d\tau$$

$$= (1/2) \int (s p_x + p_x p_x + p_y p_x + p_z p_x) d\tau = (1/2) (0 + 1 + 0 + 0) = (1/2)$$

c) Since $\int (h_1) (h_2) d\tau = 0$, h_1 and h_2 are orthogonal. (In fact, $\int (h_i) (h_j) d\tau = \delta_{ij}$)

d) Since $\int (h_1) (p_x) d\tau = (1/2)$, h_1 is not orthogonal to p_x .

3) kinetic energy for the nuclei = 3 (one for each hydrogen atom, one for the oxygen atom)

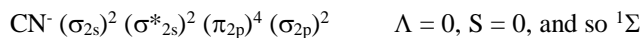
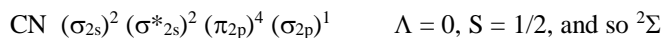
kinetic energy for electrons = 10 (one term for each electron)

nuclear-nuclear potential energy = 3 ($H_A - O$, $H_B - O$, and $H_A - H_B$)

nuclear-electron potential energy = 30 (10 terms for H_A , 10 for H_B , and 10 for O)

electron-electron potential energy = 45 (one term for each possible pair of electrons)

4) Using the molecular orbital diagram for homonuclear or heteronuclear diatomic molecules (and the rules for determining g or u symmetry, when appropriate)



Note that g/u symmetry does not apply to heteronuclear diatomic molecules or ions.

- 5) a) ${}^2\Pi_g \rightarrow {}^2\Pi_u$ allowed
 b) ${}^1\Sigma_g^+ \rightarrow {}^1\Delta_g$ forbidden ($g \rightarrow g$ is forbidden, and $\Delta\Lambda = 2$ is forbidden)
 c) ${}^3\Pi \rightarrow {}^1\Delta$ forbidden ($S = 1 \rightarrow S = 0$ is forbidden)
 d) ${}^3\Pi \rightarrow {}^3\Sigma^+$ allowed